Japan Patent Office

Kokai Patent Publication No. 119815 – 1996, May 14, 1996

Patent Application No. 287434 – 1994 Date of Application: October 26, 1994

Applicant: 592253600

K. K. Nikko

198 Miyada Kamiaki Cho Ten-o, Konan Shi, Aichi Ken

Inventor: K. Ichikawa

c/o K. K. Nikko

198 Miyada Kamiaki Cho Ten-o, Konan Shi, Aichi Ken

Attorney: M. Mukaiyama, Patent Counsel (and 1 other)

[Title of Invention] Plant germination suppressing sand, plant germination suppressing material, method of making plant germination suppressing material and method of working on the weed germination suppression

[Abstract]

[Objective] This invention provides [Constitution] The plant germination suppression sand of this invention has the coating film of aluminum oxide or silicon oxide on the surface of inorganic base material like sand, the film containing the metal or its compound having the plant germination suppression function.

[Claims of the Patent]

[Claim 1] Plant germination suppressing sand that is characterized by having, on the surface of the sand, the coating film of aluminum oxide which contains the metal or its compound having the plant germination suppressing function.

[Claim 2] Plant germination suppressing sand that is characterized by having, on the surface of the sand, the coating film of silicon oxide which contains the metal or its compound having the plant germination suppressing function.

[Claim 3] The plant germination suppressing sand described in Claim 1 or 2 in which the metal or its compound that has the said plant germination suppressing function is at least the one which is selected from silver, silver compound, copper, copper compound, zinc, zinc compound, tin, tin compound.

[Claim 4] Plant germination suppressing material that is characterized by having, on the surface of glass granules or silica gel granules, the coating film of aluminum oxide which contains the metal or its compound having the plant germination suppressing function.

[Claim 5] Plant germination suppressing material that is characterized by having, on the surface of glass granules or silica gel granules, the coating film of silicon oxide which contains the metal or its compound having the plant germination suppressing function.

[Claim 6] The plant germination suppressing material described in Claim 4 or 5 in which the metal or its compound that has the said plant germination suppressing function is at least the one which is selected from silver, silver compound, copper, copper compound, zinc, zinc compound, tin, tin compound.

[Claim 7] Method of making plant germination suppressing material, the method being characterized as follows: On the surface of one type of inorganic carrier selected from sand, glass granules, silica gel and ceramics granule, the colloidal aluminum liquid or colloidal silica liquid containing the metallic colloid of the metal that has the plant germi-nation suppressing function is contacted and, next, this is dried.

[Claim 8] The method of working on the weed germination suppression, the method being characterized as follows: At the site of working, the soil or sand is removed to a depth of 2 cm or more; at this site where the removal was done, the plant germination suppressing sand of any one of the said Claims $1 \sim 3$ or the plant germination suppressing material of any one of the said Claims $4 \sim 6$ is thrown in to a thickness of 2 cm or more.

[Claim 9] Method of working on the weed germination suppression at the tombs, the method being characterized as follows: After the base work of tombstone and the work of mounting the tombstones are finished, around the mounted tombstones, with at least 2 cm from the ground surface or the surface of tomb site area left unfilled, sand or earth is thrown in and, on the said sand or earth, the plant germination suppressing sand of any one of the said Claims $1 \sim 3$ or the plant germination suppressing material of any one of the said Claims $4 \sim 6$ is thrown in to a depth of 2 cm or more.

[Detailed Description of the Invention]

[0001]

[Field of Application in Industry] This invention is related to the plant germination sup-pressing sand, plant germination suppressing material and the method of making plant germination suppressing material. In particular, it is related to the plant germination sup-pressing material that is effective in the weed germination suppression, the method of making plant germination suppressing material and the method of working on the weed germination suppression.

[0002]

[Existing Technology] From the past, the multiplication of weeds at various places has been a problem. For the removal of this weed, numerous agricultural chemicals are used and this has become an environmental problem. Seeds of the weeds ride on the wind and scatter and germinate at the places where they fall and grow. Scattering of the seeds of weeds can not be stopped but, if the germination is suppressed, weeds do not grow.

How-ever, it is difficult to effectively suppress the germination of weeds and, for this, many agricultural chemicals are used.

[0003]

[The Problem That The Invention Intends to Solve] However, on the use of agricultural chemicals, their effects on many of the living environment are regarded as problems. Thereupon, the objective of this invention is to provide sand or germination suppression material that is like the agricultural chemical, has almost no flow out to the soil, has little change with time, can be used in various places, is safe to the environment and, also, can perform the weed germination suppression assuredly, easily and also over a long period, and the method of making them and the method of working on the plant germination suppression.

[0004]

[The Means of Solving the Problem] What achieves the said objective is the plant germi-nation suppressing sand that has, on the surface of the sand, the coating film of aluminum oxide or silicon oxide containing the metal or metallic oxide having the plant germination suppressing function.

[0005] Also, what achieves the said objective is the plant germination suppressing mater-ial that has, on the surface of glass granules, the coating film of aluminum oxide or sili-con oxide containing the metal or metallic oxide having the plant germination suppress-ing function. Also, what achieves the said objective is the plant germination suppressing material that has, on the surface of silica gel granules, the coating film of aluminum oxide or silicon oxide containing the metal or metallic oxide having the plant germination sup-pressing function.

[0006] And the said metal or its compound that has the plant germination suppressing function is preferably at least the one which is selected from silver, silver compound, copper, copper compound, zinc, zinc compound, tin, tin compound. Further, the ratio of the amount of content of the silicon oxide that is attached to the surface of the said plant germination suppressing sand or the said processed glass granules relative to the metal or its compound having the plant germination suppressing function is $10^5:1 \sim 1:1$. Also, the ratio of the amount of content of the aluminum oxide that is attached to the surface of the said plant germination suppressing sand or the said processed glass granules relative to the metal or its compound having the plant germination suppressing function is $10^4:1 \sim 4:1$.

[0007] Also, what achieves the said objective is the method of working on the weed germination suppression, the method being characterized as follows: At the site of working, the soil or sand is removed to a depth of 2 cm or more; at this site where the removal was done, any one of the said plant germination suppressing sand or the plant germination suppressing material is thrown in to a thickness of 2 cm or more. Also, what achieves the said objective is the method of working on the weed germination

suppression at the tombs, the method being characterized as follows: After the base work of tombstone and the work of mounting the tombstones are finished, around the mounted tombstones, with at least 2 cm from the ground surface or the surface of tomb site area left unfilled, sand or earth is thrown in and, on the said sand or earth, any one of the said plant germination suppressing sand or the plant germination suppressing material is thrown in to a depth of 2 cm or more.

[0008] So, now, the plant germination suppressing sand of this invention is explained. This plant germination suppressing sand has, on the surface of the sand, the coating film of aluminum oxide that contains the metal or its compound having the plant germination suppressing function. As for the sand which is used as the plant germination suppressing sand of this invention, the granular material, the so called solid material of sand form, the pulverized stone or, further, the fine powder, are used depending on the purpose. In par-ticular, the silica sand is suitable. As to the size, in terms of the granular material, the particle size of about $0.001 \sim 20$ mm is used and, suitably, it is about $0.01 \sim 10$ mm. And, on the surface of this sand, the coating film of aluminum oxide containing the metal or its compound that has the plant germination suppressing function is formed.

[0009] As for the metal or its compound having the plant germination suppressing function being used in this invention, the metal like silver, copper, zinc, tin and their com-pound are used suitably. As for the compounds, the oxides (e.g. silver oxide, copper oxide, zinc oxide, tin oxide), carbonate (e.g. silver carbonate, copper carbonate, zinc carbonate, tin carbonate), chloride (e.g. silver chloride, copper chloride, silver nitrate, zinc chloride, tin chloride), nitrate (e.g. copper nitrate, silver nitrate, zinc nitrate, tin nitrate), lactate (silver lactate, copper lactate, zinc lactate, tin lactate) are conceivable. For the strength of plant germination suppression, silver or silver compound among those described above is preferred. Further, for the safety, silver, silver oxide, silver carbonate, silver lactate are preferred.

[0010] Further, in the aluminum oxide coating film, as the metal or its compound having the plant germination suppressing function, it is preferred that different metal or the com-pound of different metal is contained. In other words, by having different metal or metal compound, it has a wider spectrum of plant germination suppression compared to the case of using only one type of plant germination suppressing metal or compound and so the plant germination suppression function becomes higher and also, the plant germina-tion suppression function is exhibited to more types of plants. And, from the view point of the plant germination suppression strength and safety, it is preferred to use silver or copper as the essential metal and at least one type of other metal (silver, copper, lead, zinc, tin, etc) (specifically, those metals or their metallic oxide carbonate, chloride, ni-trate, lactate, etc). Also, a more preferred combination is to use silver or copper as the essential metal and select 2 or more of other metals (silver, copper, lead, zinc, tin, bis-muth, etc) for use. Specific examples of preferred combination are: silver and copper, silver and zinc, silver and lead, copper and zinc, silver and zinc, silver and copper and lead, etc.

[0011] And, the main component of the sand is silicon oxide and the coating film of the aluminum that is formed on the surface is attached very solidly. And, the metal or its compound that is in the coated film and has the plant germination suppressing function is not buried completely in the coated film but it is exposed partially at the surface. Thus, the plant germination suppressing sand exhibits the function of plant germination sup-pression and anti-moss function. And, such plant germination suppressing sand can be made by contacting the surface of the sand with the colloidal aluminum liquid (alumina sol for use in plant germination suppression) containing the metal or compound having the plant germination suppression function (hereinafter, this is called the plant germina-tion suppressing metal) and then drying. And, preferably, the colloidal aluminum liquid containing the metal having the plant germination suppressing function in the form of metallic colloid is used. The said contact of the liquid with the surface of sand is conduct-ed by coating, dipping and spraying.

[0012] Alumina sol is a hydrate of alumina (aluminum oxide, Al2O3) (boehmite system) having a colloid size with the water as the dispersion medium and it is a milky white, vis-cous liquid in which polymerized particles are dispersed with the anion in water as the stabilizer. Shape of the particles is an aggregate of plumose particles and one of this plu-mose particles is formed by the polymerization of about 600,000 pieces of alumina. As to the state of the surface, the anion particles that impart the colloid stability are at the surface and its vicinity and plays the role of stabilizing the alumina particles and, also, the alumina particle itself is electrically charged positive. And, the alumina (aluminum ox-ide) has a diameter of about 10 m μ individually and a length of about 100 m μ and so its shape is approximately a cylindrical shape. As for the alumina sol, the known ones can be used and the alumina sol- 100, 200, 520. etc made by Nissan Kagaku (K. K.) can be used suitably. In particular, as for the stabilizer, that of the acetate system can be used suitably. In general, the amount of aluminum oxide contained in the alumina sol is about $5 \sim 30$ % and it contains a small amount of acid (e.g. acetic acid) as the stabilizer an, as the liquid, water is used.

[0013] And, alumina sol has the properties of coated film formability, tackiness and posi-tive electric charge. And, the alumina sol and metal or its compound can be reacted mechanochemically and, to the surface of aluminum oxide in the alumina sol, metal or its compound can be attached to make the paste type liquid substance. By coating this liquid substance to the sand and drying, the second plant germination suppressing sand of this invention is made. Alumina sol has a very large specific surface area and, because of high positive electric charge, its adsorption strength with the substance having negative charge is large and, further, as it is of a fine particle shape, it has many merits such as a high sur-face activity, reactivity, coated film formabilty and bonding characteristics.

[0014] As for the amount of aluminum oxide contained in the said alumina sol for use in plant germination suppression, it is $0.1 \sim 20$ wt %, preferably $0.1 \sim 5$ wt %. If it is below 0.1 %, there is the danger that uniform coated film may not be formed and, if it is above 20 %, the viscosity is high and there is the danger that the coating will be difficult. And, the amount of metal or its compound having the plant germination suppressing function

contained in the alumina sol for use in plant germination suppression is preferably $10^{-6} \sim 1$ wt %and, particularly preferably $10^{-3} \sim 1$ wt %. Further, in the said alumina sol for use in plant germination suppression, the ratio of content of the aluminum oxide relative to the metal and its compound having the plant germination suppression function is prefer-ably 10^6 :1 ~ 1 :1 and more preferably 10^6 :1 ~ 4 :1. And, as for the dispersion medium in the alumina sol for use in the plant germination suppressing of this invention, the water which is also a dispersion medium of alumina sol is used suitably. Also, other than water, one can use the organic solvents (e.g. acetone, dimethyl formamide, methyl ethyl ketone, also the alcohols such as methyl alcohol, ethyl alcohol and, further, ethylene glycol) and, further, the mixture of water and these substances can be used,. Also, a small a mount of PVA, PVP may be contained in the dispersion medium,

[0015] And, it is preferred that, on the surface of aluminum oxide, the metal or its com-pound (e.g. silver compound) for plant germination suppression is adhering. As for the theory of adhesion between the two, for example, when silver carbonate is used as the silver compound, a part becomes Ag₂O and a part becomes the state of Ag (colloid) and, also, a part remains as Ag₂CO₃ and is sticking to the surface of aluminum oxide by the intermolecular attraction between the two. And the adhesion strength is not that strong. And, the adhesion means that, at the surface of aluminum oxide, silver compound is contacting and is at very close distance. And, it is preferred that all of the silver com-pound contained in the aluminum sol for use in plate germination suppression is sticking to the aluminum oxide but it is all right even if a part of it is not sticking. And, preferably, the silver compound contacts the aluminum oxide and has entered between the aluminum oxide of the aggregate of aluminum oxide that is a plumose particle as said above. When it is in such a state, the coated film for use in plate germination suppression in a state where the silver compound is taken inside the aluminum oxide coated film that is formed after the coating and drying and the silver compound does not easily separate from the coated film and it exhibits the plant germination suppression strength over a long period.

[0016] And, in the alumina sol for use in the plant germination suppression, it is preferred that the metallic compound for use in plant germination suppression (e.g. silver com-pound is sticking to the surface of aluminum oxide. As to the method for this, it can be done by placing the prescribed amounts of alumina sol and silver compound in a contain-er (e.g. mortar) and, while pressing and stirring (mix- kneading), pressing the silver com-pound forcibly to the surface of aluminum oxide. Further, by pressing the silver com-pound more strongly to the surface of aluminum oxide forcibly, it is possible to have the silver compound enter between the aluminum oxides of the aggregate of aluminum oxide that are the plumose particles.

[0017] When dried, the alumina sol for use in plant germination suppression becomes a strong, coated, solidified substance of alumina having the plant germination suppression function. And, by the silver compound that is exposed at the surface of the coated, solidi-fied substance that is formed, the surface of the plant germination suppressing sand

always maintains a high level of plant germination suppression function. As to the method of said drying, keeping it at the normal temperature is all right but, preferably, it is preferred to heat for drying at a high temperature of $150 \sim 700$ deg C, more preferably $200 \sim 500$ deg c. For the drying at such a high temperature, for example, the method of using a dryer, or the method of blowing hot air to the coated surface using an industrial dryer are conceivable. Also, the separation of the silver compound sticking to the surface of sand can be suppressed strongly to prevent the occurrence of the separation of silver compound. For this, a method is to form, on the surface of the coated film of aluminum oxide containing the metal or its compound having the plant germination suppression function formed on the surface of sand, a thin coated film of aluminum oxide or silicon oxide that does not contain the metal or its compound which has the plant germination suppression function.

[0018] For this method, as the first liquid, the alumina sol having the plant germination suppressing function by containing the metal or its compound that has the plant germina-tion suppressing function in the alumina sol is coated and, after this alumina sol for plant germination suppression is solidified, as the second liquid, the simple alumina sol that does not contain the metal or its compound that has the plant germination suppression function is coated. The aluminum oxide content in the first liquid (alumina sol for plant germination suppression) is $0.1 \sim 20$ wt %, preferably $0.1 \sim 5$ wt %. The aluminum oxide

content in the second liquid is $0.01 \sim 5$ %, preferably $0.01 \sim 1$ %. By doing this, the flow out of the metal or its compound for plant germination suppression from the plant germi-nation suppressing sand is suppressed and, also, the plant germination suppression function by the silver compound which is exposed partially from the surface of the coat-ing film for the plant germination suppression can be maintained over a long period and, at the same time, the coating film of the coated surface for the plant germination suppre-ssion that is formed becomes strongly solid. Further, as the second liquid, in place of alumina sol, the silicana sol that is to be described later may be used.

[0019] Next, explanation is given on the second plant germination suppressing sand. The plant germination suppressing sand of this invention has, on the surface of the sand, the coated film of silicon oxide containing the metal or its compound that has the plant germ-ination suppression function. This plant germination suppressing sand has, on the surface of the sand, the coated film of silicon oxide containing the metal or its compound that has the plant germination suppression function. The difference between this second plant germination suppressing sand the previously described first plant germination suppress-ing sand is that the coated film formed on the surface of sand is formed by aluminum oxide in the first one and, in the second one, it is formed by silicon oxide. Regarding other points, e.g. the sand that is the carrier and the metal or its compound having the plant germination suppression function being used, they are same and those described above are used suitably.

[0020] Main component of the sand is silicon oxide and the coated film of silicon oxide formed on the surface is bonded strongly. And, the metal or its compound having the

plant germination suppression function that is in this silicon oxide coated film is not buried in the film altogether and at least a part, preferably most part, is exposed partly at the surface. By this, the plant germination suppressing sand exhibits the plant germina-tion suppressing function and the anti- moss function. In other words, in the coated film that is formed on the surface of the plant germination suppressing sand of this invention, the metal or its compound having the plant germination suppressing function exists partly in the inorganic coated film formed into the matrix by the silicon oxide and, at least a part of it is exposed at the surface.

[0021] And, such plant germination suppressing sand can be made by having the surface of the sand contact the colloidal silica liquid containing the metal or compound having the plant germination suppression function (hereinafter, this is called the plant germina-tion suppressing metal) (coating of the liquid) and, next, drying. The said contact of the liquid to the sand surface is conducted by coating, dipping or spraying. And, for the metal that has the plant germination suppression function, it is preferred to use the silica sol containing it in the form of metallic colloid (e.g. colloidal silica liquid, methyl silicate, ethyl silicate). Colloidal silica, i.e. silica sol, is the hydrate (boehmite system) of the silica (silicon oxide) having a size of colloid in the dispersion medium of water or alcohol and it is a milky white, viscous liquid in which polymerized particles are dispersed stably. Methyl silicate and ethyl silicate are the hydrolyzed product of organo siloxane that were hydrolyzed by the alcohol such as methyl alcohol, ethyl alcohol, isopropyl alcohol and it substantially has the structure of Si(OH)₄.

[0022] As for the silica sol, the known ones can be used. For example, as the one that uses water as the dispersion medium, there is the colloidal silica of Nissan Kagaku (K. K.) (trade name Snowtex); as the one that uses alcohol as the dispersion medium, there is ethyl silicate (Nippon Monsanto K. K., trade name Sil-ester); and there is the hydrolyzed ethyl silicate (Nippon Monsanto K. K., trade name: Hydrolyzed Sil-ester). These can be used suitably. Silica sol has the properties such as the coating film formability, adhesion, negative electric charge. And, by adding into this silica sol of liquid form the metal or its compound having the plant germination suppression function, the silica sol for use in plant germination suppression is prepared. More preferably, the metal for plant germina-tion suppression is made into the metallic colloid state and this is added into the silica sol. By doing so, the bonding of the metal and silicon oxide becomes strong. This is believed to be due to the dehydration bonding between the metallic colloid and silicon oxide.

[0023] Further, the silica sol and plant germination suppressing metal are reacted mecha-no-chemically to bond the metal or its compound to the surface of silicon oxide in the silica sol and form the paste type liquid substance (hereinafter, this is called the plant germination suppressing silica sol). By coating this liquid substance to the sand and dry-ing, the plant germination suppressing sand of this invention is formed. Silica sol has a very large specific surface area and, also, because of its high positive electric charge, the adsorption strength of the substance having negative electric charge is large. Further, as it is in the form of fine particles, it has many merits such as high surface activity,

reactivity, coating film formability and bonding characteristics. Further, main component of the sand is silicon oxide and so the adhesion to the sand is good and, also, as the metal and its compound exists in the silica that formed the coating film, it exhibits the plant germina-tion suppressing function and anti- mold function effectively over a long period. In gene-ral, the silicon oxide content in the silica sol is about $5 \sim 30$ % and, as a small amount of stabilizer, the water containing acid (e.g. hydrochloric acid) is used as the dispersion medium and also the alcohol containing a very small amount of acid is used as the disper-sion medium.

[0024] The silicon oxide content in the silica sol for use in plant germination suppression being used in this invention is $0.1 \sim 20$ wt %, preferably $0.1 \sim 5$ wt %. If it is below 0.1 %, there is the danger that the uniform coated film is not formed and, if it is over 20 %, the viscosity is high and the coating is difficult in some cases. The amount of metal or its compound having the plant germination suppression function contained in the silica sol for plant germination suppression is $10^{-5} \sim 10$ wt % preferably and, more preferably, it is $10^{-3} \sim 1$ wt %. Further, the ratio of the content of the metal or its compound having the plant germination suppression function and the silicon oxide in the said silica sol for use in plant germination suppression is preferably 10^{5} : $1 \sim 1$:1 and more preferably 10^{4} :1 ~ 4 :1. And, as for the dispersion medium in the silica sol for use in the plant germination suppression in this invention, the water that is the dispersion medium of silica sol is used suitably. Also, other than water, the organic solvent (e.g. acetone, dimethyl formamide, methyl ethyl ketone, or the alcohol such as methyl alcohol, ethyl alcohol, and also ethyl-ene glycol can be used. Further, the mixture of water and them may be used.

[0025] As for the mode of adhesion of the plant germination suppressing metal (e.g. silver compound) to the surface of silicon oxide, the adhesion in the form of partially being dotted is good. As to the theory of adhesion between the two, for example, when silver carbonate is used as the silver compound, a part becomes Ag₂O and a part goes into the state of Al (colloid) and also a part remains as Ag₂CO₃ and sticks to the surface of silicon oxide by the intermolecular attraction of the two. And this adhesion strength is not that strong. And the sticking indicates that the silver compound is in contact with the sur-face of the silicon oxide and that it is in a very close distance. And, it is preferred that all of the silver compound contained in the silica sol for plant germination suppression is sticking to the silicon oxide but, a part of it may be not sticking. And, preferably, the silver compound is in contact with the silicon oxide and, at the same time, it has entered between the silicon oxides of the aggregate of silicon oxide. When it is in such a state, there is formed the coating film for plant germination suppression in a state where the silver compound is taken inside the coating film of silicon oxide that is formed after the coating and drying. Thus, the silver compound does not separate easily from the coated film and the plant germination suppressing strength is exhibited over a long period.

[0026] And, it is preferred that the silver compound is sticking to the surface of silicon oxide in the silica sol. By doing so, separation of the silver compound from the coated film of silicon oxide formed on the surface of sand can be suppressed and, also, the

ex-posure of silver compound to the surface increases. As to the method for this, the pres-cribed amounts of silica sol and silver compound are placed in a container (e.g. a mortar) and this is stirred while pressing (mix-kneading) and the silver compound is pressed forcibly to the surface of silicon oxide. By pressing the silver compound more strongly to the surface of silicon oxide forcibly, the silver compound can be let to enter between the silicon oxides of the aggregate of silicon oxide. And, when dried, the silica sol becomes the strong, coated solidified material of silica (silicon oxide). And, by the silver com-pound that is exposed at the surface of the coated solidified material formed, the surface always maintains a high plant germination suppressing function. As to the method of doing described above, keeping it at the normal temperature is good but, it is preferred to conduct the drying by heating at a high temperature of preferably at 150 ~ 700 deg C, more preferably at 200 ~ 500 deg C. For such drying at a high temperature, the method of using a dryer, and also a method of blowing hot air by using a industrial dryer to the coated surface are conceivable. And, in terms of forming this coated film, particularly in terms of forming the coated film that has sufficient hardness and strength even without using a too high temperature, the hydrolyzed ethyl silicate is preferred as the silica sol.

[0027] Further, separation of the silver compound which bonded to the surface of sand is strongly suppressed so that almost no separation of the silver compound would occur. For this, on the surface of the coated film of silicon oxide containing the metal or its com-pound that has the plant germination suppression function formed on the surface of the sand, the thin coated film of silicon oxide that does not contain the metal or its compound having the plant germination suppression function is formed. For the method for this, as the first liquid, the silica sol having the plant germination suppressing function in which the metal or its compound having the plant germination suppression function is contained in the silica sol is coated and, after solidifying this silica sol for the plant germination suppressing, as the second liquid, the simple silica sol that does not contain the metal or its compound having the plant germination suppressing function is coated. As to the sili-con oxide content in the first liquid (silica sol for plant germination suppression), it is $0.1 \sim 20$ wt %, preferably $0.1 \sim 5$ wt %. As to the silicon oxide content in the second liquid, it is $0.1 \sim 5$ %, preferably $0.01 \sim 1$ %. By doing so, the flow out of the metal or compound for plant germination suppressing from the plant germination suppressing sand is suppre-ssed and, also, by the silver compound that is partially exposed from the surface of the plant germination suppressing coated film, the plant germination suppressing function can be maintained over a long period and, at the same time, the coated film on the surface of plant germination suppression function becomes more strong. Further, as the second liquid, in place of the silica sol, the alumina sol described above may be used, too.

[0028] Also, in order to improve the adhesion of the silica sol for plant germination suppression to the surface of sand, it is preferred that, after forming the coated film of aluminum oxide described above on the surface of sand, the silica sol for plant germina-tion suppression is bonded. As for the aluminum oxide that is bonded in advance to the surface of sand, the simple alumina sol that does not contain the said metal or its

com-pound having the plant germination suppression function can be used suitably. The alu-inum content in the alumina sol for this surface treatment is, $0.01 \sim 5$ %, preferably $0.01 \sim 1$ %.

[0029] Next, explanation is given on the plant germination suppressing material of this invention. The plant germination suppressing material of this invention has the coated film of aluminum oxide containing the metal or its compound that has the plant germi-nation suppression function on the surface of the glass granules. As for the glass granules that is used in the plant germination suppressing material of this invention, the granules, beads, the so called sandy solid material, glass pulverized product, and fine powder are used depending on the purpose. As to the size, in terms of the granular material, the particle size of about $0.001 \sim 20$ mm is used and, suitably, it is about $0.01 \sim$ 10 mm. Also, for the glass granules, a reused material can be used and, depending on the usage, a colored material can be used, also. And, at the surface of the glass granules, there is the coated film of aluminum oxide containing the metal or its compound that has the plant germination suppression function. The difference between this plant germination sup-pressing material and the first plant germination suppressing sand described above is the difference of carrier materials. As to the aluminum oxide coated film that is formed and the metal or its compound that has the plant germination suppression function which is used, they are same and the materials described above can be used suitably.

[0030] The second plant germination suppressing material of this invention has, on the glass granules, the coated film of silicon oxide containing the metal or its compound that has the plant germination suppression function. As for the granular materials that are used in the plant germination suppressing material of this invention, those described above can be used suitably. And, at the surface of this plant germination suppressing material, there is the coated film of silicon oxide containing the metal or its compound that has the plant germination suppression function. The difference between this plant germination suppre-ssing material and the second plant germination suppressing sand described above is the difference of the carrier material and they are same in regard to the coated film of silicon oxide that is formed and the metal or its compound that has the plant germination suppre-ssion function and the materials described above are used suitably.

[0031] Next, explanation is given on the third plant germination suppressing material of this invention. The plant germination suppressing material of this invention has, on the surface of the silica gel granules, the coated film of aluminum oxide containing the metal or its compound that has the plant germination suppression function. As for the silica gel granules that is used in the plant germination suppressing material of this invention, the granules, beads, the so called sandy solid material, the pulverized material and, further, fine powder are used depending on the purpose. Specifically, in terms of granular material, that having a particle size of about $0.01 \text{ mm} \sim 20 \text{ mm}$ is used, and suitably, it is about $0.01 \sim 10 \text{ mm}$. And, at the surface of this plant germination suppressing material, there is the coated film of aluminum oxide containing the metal or its compound that has

the plant germination suppression function. The difference between this plant germination suppressing material and the first plant germination suppressing sand is the different ce of the carrier material and, as to the coated film of aluminum oxide formed and the metal or its compound having the plant germination suppression function which is used, they are same and the materials described above are used suitably.

[0032] The fourth plant germination suppressing material has, on the surface of silica granule, the coated film of silicon oxide containing the metal or its compound that has the plant germination suppression function, As for the silica gel granules that is used in the plant germination suppression material of this invention, those described above are used suitably. And, at the surface of this plant germination suppressing material, there is the coated film of silicon oxide containing the metal or its compound that has the plant germination suppressing material and the second plant germination suppressing sand described above is the difference of the carrier material. And, as to the coated film of silicon oxide formed, the metal or its compound that has the plant germination suppressing function that is used, they are same and those described above are used suitably.

[0033] Further, the said plant germination suppression material can be made by contact-ing the surface of the glass granule and silica gel with the colloidal aluminum liquid or colloidal silica liquid containing the metal or its compound that has the plant germination suppressing function and, next, drying this. Further, preferably, to the surface of glass granules and silica gel, the colloidal silica liquid or the colloidal aluminum liquid con-taining the metallic colloid of the metal that has the plant germination suppressing func-tion is contacted and, next, drying is done. Also, in place of the silica gel, one may use the ceramic granules (e.g. silica- alumina).

[0034] Next, explanation is given on the method of working on the weed germination suppression of this invention. Regarding the method of working, the case of working around the tombstones of the tombs is taken as an example and is explained. First, the explanation is given on the case of working on the existing site. First, the soil or sand of the working site (around the tombstone) is removed by a depth of about 2 cm or more, preferably 3 cm or more, and more preferably 5 cm or more and, then, in continuation, at the site of working from which the soil or sand was removed, the above described plant germination suppressing sand or the above described plant germination suppressing material is thrown in to form a layer having a depth of 2 cm or more. As for the thickness of the layer, preferably, it is more than 3 cm, more preferably more than 5 cm. By this, the work is finished. Also, in order to prevent the scattering of the plant germination suppressing sand or plant germination suppressing material that is being thrown in, the said plant germination suppressing sand or the said plant germination suppressing mater-ial is thrown in to the site of working from which the soil or sand was removed in such a way that the surface of the thrown- in material is somewhat lower than the ground sur-face. On top of the thrown- in surface of the plant germination suppressing sand (over the layer), it is preferred to mount the decorative stone such as gravel. As for the gravel, that whose size is larger than that of the plant germination suppressing sand is suitable.

[0035] Also, in the case of working on a new tomb site, first the base work for the tomb-stone and the work of mounting the tombstones are conducted and, after that, around the mounted tombstones, the sand or soil (e.g. the mountain sand) is thrown in with at least 2 cm, preferably 3 cm or more, particularly preferably 5 cm or more left from the surface of the ground or the tomb site dividing objects (e.g. the stone material for partitioning the area from the other neighboring tomb) and, on top of this sand or earth layer, any one of the above mentioned plant germination suppressing sand or the plant germination supper-ssing material is thrown in to a depth of more than 2 cm. preferably more than 3 cm, particularly preferably more than 5 cm. Further, as mentioned before, the plant germina-tion suppressing sand or the said plant germination suppressing material is thrown in such a way that the surface of the thrown in material is somewhat lower than the ground sur-face. And, it is preferred that, on top of the surface of the thrown in material of this plant germination suppressing sand (on the layer), the decorative stone like gravel is mounted. As for the gravel, that whose size is larger than that of the plant germination suppressing sand is suitable. Also, only at the time of this working, a mall amount of agricultural che-mical may be sprayed. As to the spraying of the agricultural chemical, it is preferred to conduct it before throwing in of the said plant germination suppressing sand. But, it may be done after the plant germination suppressing said is thrown in, or after the mounting of the said decorative stone. By spraying the agricultural chemical in this way, even if some germinated weeds are present in the soil that was thrown in, its growth can be prevented. Also, this agricultural chemical disappears by the rain that comes after the working but, after this, even if the seeds of weeds come by flying, the plant germination suppressing sand would suppress the germination. And so, the multiplication of weeds can be pre-vented over a long period and the tomb site management is easy without the need for the work for weeding.

[0036] [Examples of Application]

(Example of Application 1) As the alumina sol, the (alumina sol- 200, aluminum oxide content about 10 %; as the stabilizer, a minute amount of acetic acid was contained; specific gravity 1.09 ~ 1.14, pH 4.0 ~ 6.0) made by Nissan Kagaku K. K. was used. As the metallic compound for use in the plant germination suppression, silver nitrate (made by Wako Jun-yaku K. K.) was used. 100 g of the alumina sol (about 110 g) and 1.7 g of the silver nitrate were put in an automatic mortar and, while pressing, stirring (pulverizing in the mortar) was done to forcibly press the silver nitrate to the surface of silicon oxide to obtain about 110 g of the alumina sol for use in plant germination suppression. As the silica sand, 1000 g of that whose particle size was in the range of 1.2 ~ 2.5 mm (made by Choko Sangyo K. K.) was used. And, 100 g of the alumina sol for use in the plant germination suppression was sprayed to the said silica sand and the silica sand was stirred well and next, it was placed in a column of rotary kiln and it was heated and dried for 10 minutes at 400 deg C to prepare the silica sand for use in the plant germination suppression in this invention.

[0037] (Example of Application 2) As the alumina sol, the (alumina sol- 200, aluminum

oxide content about 10 %; as the stabilizer, a minute amount of acetic acid was contained; specific gravity 1.09 ~ 1.14, pH 4.0 ~ 6.0) made by Nissan Kagaku K. K. was used. As the metallic compound for use in the plant germination suppression, silver nitrate (made by Wako Jun-yaku K. K.) was used. And, to 83 g of water, 17 g of silver nitrate was add-ed and stirred. Into the 100 g of silver nitrate water solution, 50 g of the 1 % sodium hyd-roxide water solution was added to prepare the liquid in which colloid silver was formed. As the silica sand, 100 g of that whose particle size was less than 5 mm (made by Choko Sangyo K. K.) was used. Then, 100 g of the alumina sol for use in plant germination sup-pression was sprayed to the said silica sand. After the silica sand was stirred well, it was put in the column of rotary kiln and heating for drying was done at 400 deg C for 10 min-utes to prepare the silica sand for use in plant germination suppression in this invention.

[0038] (Example of Application 3) As the alumina sol, (alumina sol -200) made by Nissan Kagaku K. K. was used. As the metallic compound for use in plant germination suppression, silver nitrate (made by Wako Jun-yaku K., K.) and copper sulfate (made by Nippon Kagaku Sangyo K. K.) were used. And, 100 g of alumina sol was diluted to 10 times with water to prepare 1000 g of dilute alumina sol. And, to 100 g of water solution prepared by adding 8.5 g of silver nitrate into 71.5 g of water and stirring, 50 g of 1 % sodium hydroxide water solution was added to prepare the liquid in which the colloid silver and colloid copper were formed. And, to 100 g of the dilute alumina sol, 1.5 g of the liquid containing the said colloid silver and copper was added and this was stirred well to obtain about 100 g of the plant germination suppressing alumina sol. As for the silica sand, 1000 g of that whose particle size was below 5 mm (made by Choko Sangyo K. K.) was used. And, 100 g of the alumina sol for use in plant germination suppression was sprayed to the said silica sand and the silica sand was stirred well. Next, it was plac-ed in a column of a rotary kiln and the heating for drying was done at 400 deg C for 10 minutes to prepare the silica sand for use in plant germination suppression in this inven-tion.

[0039] (Example of Application 4) As the alumina sol, the (alumina sol- 200, aluminum oxide content about 10 %; as the stabilizer, a minute amount of acetic acid was contained; specific gravity $1.09 \sim 1.14$, pH $4.0 \sim 6.0$) made by Nissan Kagaku K. K. was used. This alumina sol was diluted to about 10 times with water to prepare the dilute alumina sol. And, in this dilute silica sol, the processed silica sand for use in plant germination suppre-ssion of Example of Application 3 was dipped and pulled up and heating for drying was done at 400 deg C for 10 minutes to prepare the silica sand for use in plant germination suppression in this invention.

[0040] (Example of Application 5) As the silica sol, the hydrolyzed ethyl silicate (Nippon Monsanto K. K., trade name Sil Ester XAR, silicon oxide content about 20 %; ethyl alco-hol 27.5 %, isopropyl alcohol 52.5 %; as a stabilizer, a minute amount of sulfuric acid was contained; viscosity 4 cps, specific gravity 0.915; white turbid liquid) was used. As the metallic compound for use in plant germination suppression, silver nitrate (made by Wako Jun-yaku K. K.) was used. And, 100 g of silica sol was diluted to 10 times with

ethyl alcohol to prepare 1000 g of dilute silica sol. And, to 100 g of the silver nitrate water solution prepared by adding 17 g of silver nitrate into 83 g of water and stirring, 50 g of the 1 % sodium hydroxide water solution was added to prepare the liquid in which coloid silver was formed. And, to 100 g of the dilute silica sol, 1.5 g of the liquid contain-ing the said colloid silver was added and this was stirred well to obtain about 100 g of the silica sol for use in the plant germination suppression. As the sand, 1000 g of that whose particle size was below 5 mm (made by Choko Sngyo K. K.) was used. And, 100 g of the silica sol for use in plant germination suppression was sprayed to the said silica sand and next, the silica sand was stirred well. Next, it was placed in the column of rotary kiln and heating for drying was conducted at 250 deg C for 10 minutes to prepare the silica sand for use in plant germination suppression in this invention.

[0041] (Example of Application 6) As the silica sol, the same hydrolyzed ethyl silicate as that which was used in Example of Application 5 was used. As the metallic compound for use in plant germination suppression, silver nitrate (made by Wako Jun-yaku K. K.) and the copper nitrate (made by Nippon Kagaku Sangyo K. K.) were used. And, 100 g of silica sol was diluted to 10 times with ethyl alcohol to prepare 100 g of dilute silica sol. And, to 100 g of water solution prepared by adding 8.5 g of silver nitrate and 20 g of copper nitrate in 71.5 g of water and stirring, 50 g of 1 % sodium hydroxide water solu-tion was added to prepare the liquid in which the colloid silver and colloid copper were formed. And, to 100 g of the dilute silica sol, 1.5 g of the liquid containing the said colloid silver and copper was added and this was stirred well to obtain about 100 g of the silica sol for use in plant germination suppression. As the silica sand, 1000 g of that whose particle size was below 5 mm (made by Choko Sangyo K. K.) was used. And, 200 g of the silica sol for use in plant germination suppression was sprayed to the said silica sand and, next, the silica sand was stirred well and placed in the column of rotary kiln and heating for drying was conducted at 250 deg C for 10 minutes to prepare the silica sand for use in plant germination suppression in this invention (Example of Application 3).

[0042] (Example of Application 7) As the silica sol, (trade name Snowtex 0, made by Nissan Kagaku K. K., silicon oxide content about 20 %, water about 80 %; as the stabi-lizer, a minute amount of hydrochloric acid was contained; viscosity 1 ~ 3 cps, specific gravity 1.12 ~ 1.14; white turbid liquid) was used. As the metallic compound for use in plant germination suppression, silver nitrate (made by Wako Jun-yaku K. K.) and copper nitrate (made by Nippon Kagaku Sangyo K. K.) were used. And, 100 g of silica sol was diluted to 10 times with water to prepare 1000 g of the dilute silica sol. And, to 71.5 g of water, 8.5 g of silver nitrate and 20 g of copper nitrate were added and stirred. To 100 g of the water solution thus obtained, 50 g of 1 % sodium hydroxide water solution was added to prepare the liquid in which colloid silver and colloid copper were formed. And, to 100 g of the dilute silica sol, 1.5 g of the said liquid containing the colloid silver and copper was added and this was stirred well to obtain about 100 g of the silica sol for use in plant germination suppression. As the silica sand, 1000 g of that whose particle size was below 5 mm (made by Choko Sangyo K. K.) was used. And, in the silica sol for use in plant germination suppression, the said silica sand was dipped and

then pulled up and placed in the column of rotary kiln and heating for drying was conducted at 400 deg C for 10 minutes to prepare the plant germination suppressing sand of this invention.

[0043] (Example of Application 8) As the silica sol, (Snowtex 0) made by Nissan Kagaku K. K. was used and this silica sol was diluted to about 10 times with water to prepare the dilute silica sol. 100 g of this dilute silica sol was sprayed to the processed silica sand for use in the plant germination suppression of Example of Application 7 and, next, the silica sand was stirred well and then it was placed in the column of rotary kiln and heating for drying was conducted at 400 deg C for 10 minutes to prepare the plant germination sup-pressing material of this invention.

[0044] (Example of Application 9) In place of the silica sand, 1000 g of glass beads (average spherical diameter 1 mm, made by Toshin Ricoh K. K.) was used. Other than this, the same procedure of Example of Application 7 was followed to prepare the plant germination suppressing material of this invention having the silicon oxide film contain-ing the silver compound and copper compound on the surface.

[0045] (Example of Application 10) In place of the silica sand, 1000 g of silica gel (average spherical diameter 1 mm, made by Toshin Ricoh K. K.) was used. Other than this, the same procedure of Example of Application 7 was followed to prepare the plant germination suppressing material of this invention having the silicon oxide film contain-ing the silver compound and copper compound on the surface.

[0046] (Example of Application 11) In place of the silica sand, 1000 g of glass beads (average spherical diameter 1 mm, made by Toshin Ricoh K. K.) was used. Other than this, the same procedure of Example of Application 3 was followed to prepare the plant germination suppressing material of this invention having the silicon oxide film contain-ing the silver compound and copper compound on the surface.

[0047] (Example of Application 12] In place of the silica sand, 1000 g of silica gel (average spherical diameter 1 mm, made by Toshin Ricoh K. K.) was used. Other than this, the same procedure of Example of Application 3 was followed to prepare the plant germination suppressing material of this invention having the silicon oxide film contain-ing the silver compound and copper compound on the surface.

[0048] [Experiment]

[Experiment 1] Over an area of about 1 m² of ground surface, the earth and sand were removed to a depth of more than 2 cm. And, the plant germination suppressing sand of Example of Application 1 was thrown in to a depth of about 3 cm. The sand that was thrown in was about 48 kg. And, this was left still for 12 months and no multiplication of weeds was seen.

[0049] (Experiment 2] Over an area of about 1 m² of ground surface, the earth and sand

were removed for a depth of more than 5 cm. And, to about half of this site, the plant germination suppressing sand of Example of Application 1 was thrown in to a depth of about 5 cm. The sand that was thrown in was about 40 kg. Also, to the remaining half, the sand that was used in Example of Application 1 (untreated sand) was thrown in to a depth of about 5 cm. And, about 5 g of the seeds of weeds that was collected was sprayed all over the site where the sand was thrown in. After this, water was sprayed and then the site was left still for 12 months. As the result, at the site where the germination suppre-ssing sand of Example of Application 1 was thrown in, multiplication of weeds was not seen but, at the site where the simple sand was thrown in, multiplication of may weeds was confirmed.

[0050]

[Effectiveness of the Invention] The plant germination suppressing sand and the plant germination suppressing material of this invention have, on the surface of sand, the coated film of aluminum oxide or silicon oxide containing the metal or its compound that has the plant germination suppression function and, consequently, by throwing the presc-ribed amount of it to the prescribed site, it suppresses the germination of the seeds of weeds when they are present at the site or come flying to the site. Therefore, there is no need for the weeding work and the land management is made easy. This suppressing sand and suppressing material is effective around the tombs, street trees and the median sepa-ration zone of the road where the earth and trees exist and the weeding work is not easy. Also, as the metal or its compound that has the plant germination suppressing function is arrested in the coated film of silicon oxide or aluminum oxide, it does not flow out easily and does not fall off. Consequently, it is safe to the environment and, at the same time, it exhibits the effect over a long period. Also, the method of working on the weed germina-tion suppression of this invention removes the soil or sand at the working site to a depth of 2 cm or more and the said plant germination suppressing sand or the plant germination suppressing material is thrown in to a thickness of 2 cm or more at this site and so the work is very easy.